Title: Literature Review of Spin On Glass

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Literature Review of Spin On Glass

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Spin on glass (SOG) is a promising material that combines the planarization properties of a low-viscosity liquid with a dielectric constant lower than that of silicon dioxide. However, as this paper will show, this material comes with significant processing and material properties challenges that must be understood and overcome. Significant research has been accomplished through a variety of processing techniques that will be reviewed here.

Introduction

As the dimensions of integrated circuit (IC) fabrication become smaller and smaller, the demands placed upon materials used for their construction are beginning to exceed the capabilities of said materials. This has inspired a search for new materials with better performance which unfortunately commonly encounter unique problems. A well-known example of this is the integration of copper into today's IC structures. Copper has, among other properties, improved electrical conductivity, but suffers from a propensity towards migration, causing industry leaders to redesign entire IC fabrication plants around the need to keep copper contained.

Another set of common problems are the issues of planarization and insulation. Planarization is the reduction of distances between topography extremes in the direction orthogonal to the wafer, and the reduction of the slopes of side-walls. By creating a more even plane, future IC operations possess improved adhesion and quality, and planarization has established itself as a necessary facet of IC manufacturing. Insulation is the construction of insulating layers which are used in the design of all IC structures. In the past this has been commonly accomplished by thermally oxidizing silicon; however, for some applications the miniaturization desired means the thicknesses that silicon dioxide's dielectric constant requires to prevent unwanted current transfer or leakage are no longer acceptable.

SOG is a material that can serve as both a planarization agent and an insulation layer. SOG can be spin coated onto a wafer and then hardened into glass by curing. This forms air filled pores and insulating organic terminal groups within the SOG[1], which can create dielectric constants as low as 1.9[2] and thicknesses on the scale of up to a couple micrometers. However, these pores also reduce the material strength properties of the SOG, and can cause an increased susceptibility to cracking and water induced corrosion. The SOG loses a significant amount of material through thermal decomposition and also has a thermal expansion coefficient that differs from that of silicon and silicon dioxide, which leads to significant tensile stresses when thermally curing[3].

Material Composition and Application Procedures

SOG is composed of a low molecular weight organic group, such as H, OH, or CH_3, bonded to a silicon backbone and dissolved in an alcohol[1,2]. A variety of polymers

can be added to change dielectric constant, strength, and durability, among other properties[4].

Application onto a substrate is performed by using the well-known spin coating technique. A sufficient amount of SOG is placed onto a wafer using a dropper. The wafer is then spun at high speed to evenly distribute the SOG over the wafer using centrifugal force. The low viscosity of the SOG enables it to fill trenches and other gaps that may be present on the wafer. Specific spin on procedures vary; a few authors add a lower speed spin step of a couple hundred RPM for about a minute, but all authors agree on a spin of a couple thousand RPM for about a minute[2,3,4]. This generates a thin film with uniformity generally within less than 5%[5,6] across the wafer.

In the curing procedure, there is first a low temperature soft cure which serves to evaporate most of the alcohol. This changes the film from a liquid to a gel and improves stability. Next there is a high temperature hard cure which evaporates the rest of the alcohol and some of the organic groups. The evaporated organic groups leave behind air-filled pores of varying size, which generally decrease the dielectric constant but also decrease the strength properties of the film. Thus the final properties of the film can be further tuned by modifying the cure temperature and time by changing the thermal decomposition of the organic groups.

To explore the modifications that can be made by varying the cure parameters, authors have experimented with a wide variety of thermal cure procedures. A smaller number of explorations have been made into using non-thermal cure procedures. These will be discussed later in the paper. As an example to the reader, some of the thermal curing procedures and their results are summarized in Figures 1.
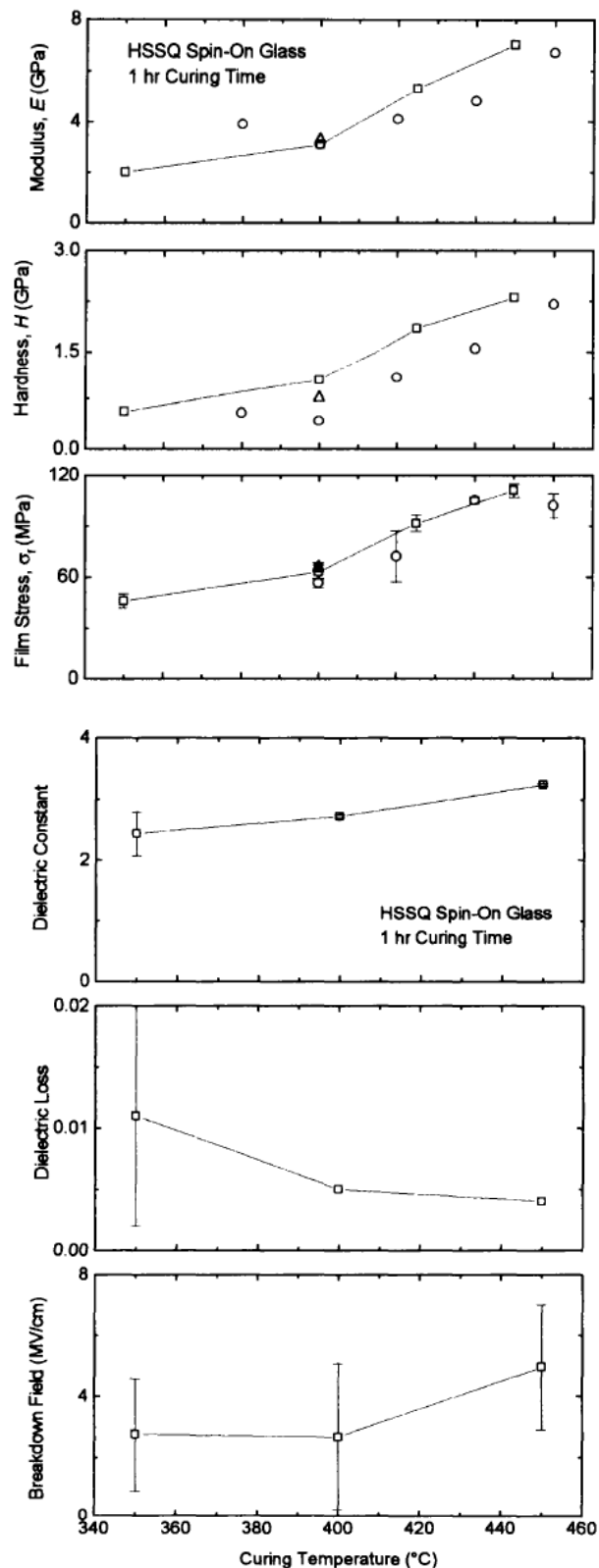

Figure 1. Dielectric constant, dielectric loss, and dielectric

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breakdown as a function of curing temperature at fixed curing time[6].

Challenges

The greatest challenge in using SOG is that the difference in thermal expansion coefficient of silicon (2.6 μm C^{-1}) or silicon dioxide (0.56 μm C^{-1}) and SOG (5 μm C^{-1}) can lead to considerable stress imposed on the SOG as it expands quicker than its substrate[5]. The SOG is allowed to expand and contract in the direction perpendicular to the wafer plane, but at the interface between the thin film and the substrate considerable tensile stress can occur in the direction parallel to the wafer plane[5]. This can cause undesirable cracks to form in the SOG, which impair insulation, adhesion, and planarization. Additionally, these cracks are hot spots for corrosion and crack growth, which further degrade the capabilities of the thin film.

The choice of organic group can drastically affect the ability of the SOG thin film to resist initial cracking and the formation of additional cracks. Use of a hydrogen group can cause unstable fragmentation and rapid extension of cracks even after being exposed to moist air, whereas other organic groups such as methyl or phenyl displayed greater resistance to cracking and water based corrosion[6].

A simpler way of increasing the durability of the thin film is by reducing the thickness of the layer. Thicker layers show worse adhesion, higher crack formation, and higher crack growth than thinner films[6]. Thinner layers can be made using greater spin on speeds or lower concentration of organic groups and silicon within the alcohol solvent.
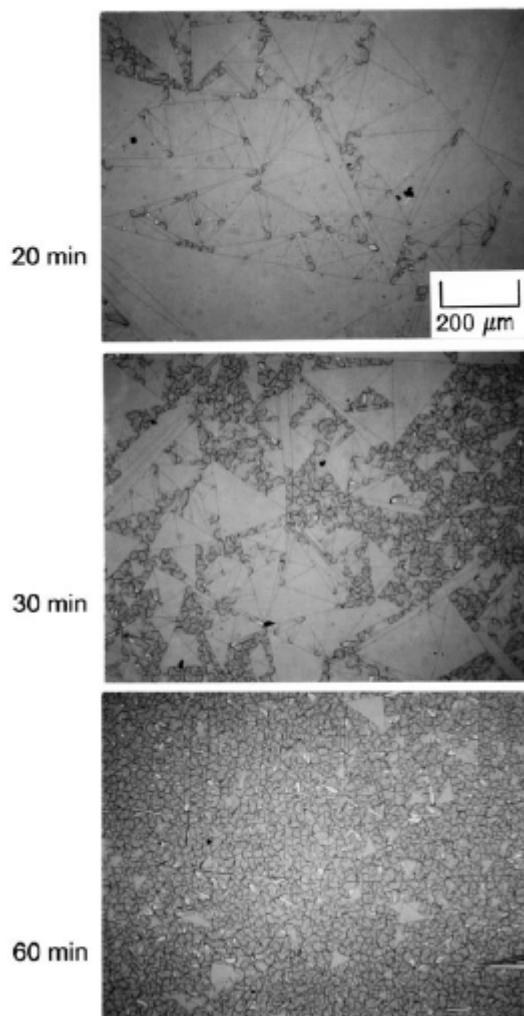

Figure 2. SOG thin film 1μm thick is placed in water and undisturbed for variable time. Cracks form and grow[6].

Control of Properties through Material Composition

As mentioned above, many of the properties of SOG can be effectively manipulated by changing the composition of the SOG. The goal of most of these additives is to modify the glass network end product for higher strength, lower dielectric constant, or other desirable traits.

Many times different polymers are added to SOG. These polymers

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can widely vary in composition and effect; for example, adding a polynorbornene to act as a sacrificial polymer can create large air gaps by thermally decomposing and further drop the dielectric constant to 2.3 or less[4,7]. However, these additional gaps (or pores) can also greatly reduce the material strength properties of the thin film. For example, the Young's modulus can be reduced from about 2.75 GPa for pure SOG to 1.75 GPa and hardness is reduced from 0.5 GPa to 0.05 GPa when 30% by weight of the polymer trimethoxysilyl norbornene (TMSNB) is added to the SOG[8]. Polyimide derivatives can be added that improve stability in the face of corrosion effects of moist air or water[3], which prevents the formation of cracks and crack growth.

A more exotic change can be made by adding dyes to the SOG solution[9]. The dye will act as an anti-reflective layer that can be tuned to a variety of wavelengths by adding different dyes. This prevents a common problem with photolithography where UV light can pass through deposited photoresist, through the underlying silicon dioxide, and reflect off the silicon substrate. Upon returning to the photoresist, the light will interact and cause unwanted defects in the areas of the photoresist outside of the intended pattern, degrading the quality of the photolithography. A layer of SOG deposited on top of the silicon dioxide with UV light absorbing dye will stop the UV light and prevent it from reflecting back into the photoresist while still serving as a useful planarizing, insulating layer than can be etched like normal glass.
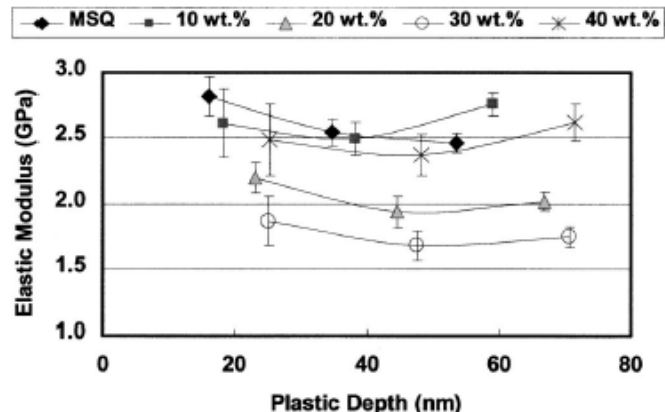

Figure 3. Effect of adding porogen polymers to SOG thin films on the elastic modulus[8].

Control of Properties through Curing Procedure

A curing procedure with higher temperatures or longer times will thermally decompose a greater amount of the organic groups. This generally increases the dielectric constant, reduces the level of porosity by encouraging the growth of O-Si-O, increases Young's modulus by removing the air filled gaps, increases hardness, and increases film stress[6,7,10]. If differing polymers are present, higher temperatures may also encourage beneficial or detrimental interactions between those polymers.

Generally the curing procedure removes different materials at different temperatures with corresponding changes in density of the thin film. At up to about 200 °C, the main loss is that of the solvent evaporating. From 250 to 350 °C, the structure of the SOG changes from a cage like structure to a more bonded network one. At temperatures greater than 435 °C, the pore network collapses and is replaced by an extensive Si-O-Si network[10].

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Increased organic content will exponentially decrease the buffered oxide etch (BOE) etching rate of SOG[11]. Thus it is possible to control the etch rate of the thin film by reducing or increasing the cure temperature or time to manipulate the thermal decomposition of the organic content. As shown in Figure 3, the wet etch rate can be managed to be as high as 10000 Å/min to as low as 500 Å/min, a difference of a factor of 20.
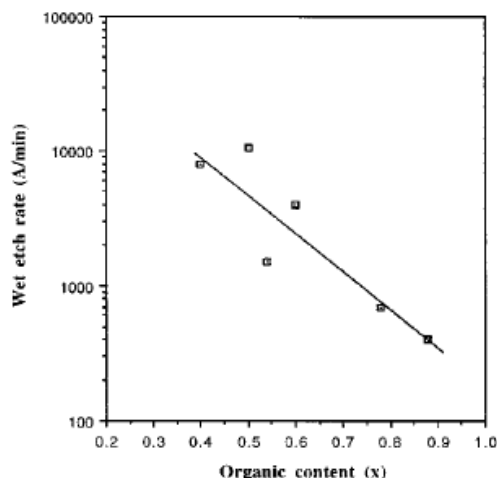

Figure 4. Wet etch rate as a function of organic content showing exponential decrease in etch rate as organic content increases[11].

To avoid the cracking induced by differing thermal expansion coefficients of the thin film and the substrate, various curing procedures have been explored that do not use heat. Wide solid angle electron beam radiation combined with infrared heating lamps can be used to eliminate organic groups and the solvent with temperatures of under 250 °C[12]. Low wavelength laser scanning can cure specific organic groups by using photothermal and photochemical mechanisms that have limited interaction with the Si-O-Si and silicon dioxide formations[13], while the solvent can be evaporated out with low temperature thermal curing.

Alternative Uses

SOG can be utilized for a variety of different purposes beyond simple planarization and insulation. A very simple property that can be taken advantage of is the different BOE rate that SOG has over silicon dioxide. The higher wet etch rate of SOG of 10000 Å/min can be used to preferentially expose areas on a wafer while still covering other areas with silicon dioxide or can be used to decrease the amount of time spent in a wet etch bath. Alternatively, the etch rate can be lowered to 500 Å/min and the SOG can be deposited to protect specific areas, fill trenches, and cover up defects. As has been previously mentioned, a layer of SOG can serve as an anti-reflective coating to protect photoresist from reflected UV light[9]. A layer of pre-cure liquid SOG can have a specific pattern imprinted by a nanoimprint lithography device similar to a printing press[14]. These patterns can form lines as thin as 10 nm and can be transferred to Au and Si by standard liftoff techniques. They can also be imprinted at room temperature, which is an advantage over other patterning substances such as poly(methyl methacrylate) (PMMA) which must be heated before imprinting can take place and incur significant deformities when cooling[14].

A more complicated technique is using atomic force microscopy to perform nanometer scale lithography to make very detailed and precise patterns. This is done by driving the probe over areas that the operator desires to keep. The electric field of the probe tip selectively oxidizes the closest area of the SOG, while the electrons of the probe tip decompose nearby organic groups. The resulting oxidized areas have a lower etch rate than the unoxidized

areas, which allow the pattern to be exposed through etching[11].

Conclusion

This paper demonstrates that SOG can be used for next generation IC manufacturing thanks to its beneficial properties of planarization and insulation. Although there are many material challenges to overcome, such as low material strength and susceptibility to water based corrosion, SOG is a viable replacement for silicon dioxide in novel IC design of the future.

A considerable challenge to the adoption of SOG is its low mechanical performance and corrosion resistance. Many techniques exist to improve upon these shortcomings, such as reducing cure temperature, curing with methods other than thermal heating, and adding specific polymers to the SOG that either create air filled gaps at lower temperatures or construct a stronger network.

There are many ways to modify the properties of SOG. The simplest is by varying the cure time and temperature. More complicated methods include adding different polymers or dyes to improve performance or add new capabilities.

Of interest is the alternative ways that SOG can assist in the IC manufacturing process. SOG can be used to craft delicate patterns on wafers either through nanoimprint lithography or with atomic force microscopy. SOG can also improve photolithography resolution by preventing UV light from reflecting back into photoresist and causing undesired reactions.

Despite some less than ideal properties, SOG is a uniquely useful material that is a viable successor to the role traditionally held by silicon dioxide and has other exciting applications as well.

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